

NOTES ON SOME CHILEAN COPPER MINERALS.

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Some time ago my brother, Mr. Hermann A. Keller, presented me with a fine suite of mineral specimens collected by him on a professional trip to Chilean mining localities. The minerals, which include native sulphur and copper, various oxides, chlorides, sulphates, borates and silicates, were for the most part readily identified by their characteristic appearance or by simple tests, but some of them aroused my curiosity, partly because of their rare occurrence, and partly on account of their beauty or exceptional purity. I was thus led to make a number of qualitative and quantitative analyses, the results of which appear to me sufficiently interesting to be placed on record. In the present paper I shall confine myself to the description of some minerals containing copper as either a principal or a minor constituent.

CUPREOUS MANGANESE.

It is well known that in many varieties of psilomelane or wad the manganous oxide is partially replaced by oxide of copper, and that special names have been given to some of those varieties in which the proportion of the latter oxide is considerable. Among them is the pelocnite from Remolinos, Chile, which was first described by Richter,¹ and chemically characterized by Kersten.² Its quantitative composition, however, does not appear to have been fully determined. The material supplied by my brother included several very fine specimens of a cupreous manganese from Huiquintipa, Province of Tarapacá, and these are unquestionably identical with Richter's pelocnite. With the one exception of the specific gravity, the physical and chemical characters of the new material are precisely

¹ *Poggendorffs Annalen*, 21, 590.

² *Schweigger's Journal*, 66, 7.

similar to those of the Remolinos occurrence. The mineral is massive and amorphous, has a conchoidal fracture, a bluish-black color and a liver-brown streak. Its hardness is between 3 and 4, and the specific gravity 3.683 (instead of 2.5–2.6). When broken into small pieces and carefully picked with the aid of a lens, the material appeared quite homogeneous except for a few particles of quartz and some green or bluish specks of a copper compound on the outside and along the crevices. A qualitative analysis showed that it contains the oxides of manganese, copper and iron, together with water and varying amounts of admixed silica. To ascertain whether the mineral has a definite chemical composition analyses were made of carefully selected samples from different specimens. It was found that the silica, which separates on dissolving the substance in hydrochloric acid, is not uniformly distributed through the mass. Its percentage varied from 12 per cent. to 32 per cent., and its microscopic examination showed that it consists entirely of quartz. There could be no doubt, then, that it is simply an admixture, and that in calculating the composition, the silica (of which only a trace dissolves with the mineral) should first be deducted from the amount of the substance taken. The results of the analyses were as follows:

	I.	II.	III.	IV.
Oxygen.....	14.37%	14.18%	13.89%	not det.
Manganous oxide.....	69.61	68.95	69.44	70.61%
Cupric oxide.....	5.86	6.05	5.69	6.48
Cobalt oxide.....	.48	.56	not det.	not det.
Barium oxide.....	.36	.47	not det.	not det.
Ferric oxide.....	2.05	1.94	1.89	} 4.22
Alumina.....	1.92	1.91	2.10	
Water.....	5.14	5.29		
	99.79%	99.35%		

It is seen from these figures that the proportions of the several constituents of the mineral are fairly constant. The composition is that of psilomelane, in which part of the manganese is replaced by copper. It is difficult to account for the very constant proportions of oxide of iron and alumina.

Regarding the determinations of water and of available oxygen, I may mention that the former was made by heating the substance

in a current of dry air and collecting the moisture in calcium chloride, while the latter was estimated iodometrically in I. and II., and indirectly in III., by heating a weighed portion, first in air and then in hydrogen, and allowing for the water and the reduction of the oxides of copper and iron. As a matter of course this method is less reliable, but the result nevertheless agrees quite well with the iodometric determinations.

CHALCANTHITE AND A DOUBLE SULPHATE OF COPPER AND MAGNESIUM.

Among the specimens that claimed my special attention there was one³ consisting of irregular and rounded masses, and which was labeled "sulphate of copper and aluminium." While the shape of the little lumps was about the same, three distinct kinds of material could readily be picked from the specimen, even without the help of a magnifying glass.

One of these substances had a deep blue color and was recognized without difficulty as chalcantbite. The blue masses were evidently crystals which were strongly corroded and slightly effloresced on the surface. A quantitative analysis confirmed the composition $\text{CuSO}_4 + 5\text{H}_2\text{O}$, with very small amounts of iron and magnesium sulphates, and a slight admixture of silicious matter. It gave:

	Found. Per Cent.	Calculated. Per Cent.
Sulphur trioxide	32.21	32.1
Cupric oxide	31.52	31.8
Ferrous oxide30	
Magnesium oxide35	
Water	35.79	36.1
	<u>100.19</u>	<u>100.0</u>

More interesting were the bluish-white masses which formed the larger portion of the specimen. They were earthy and friable, but presented shapes and surfaces exactly similar to those of the chalcantbite, suggesting a pseudomorph after the latter. In composition, however, the material was found to differ from chalcantbite in

³ From Copaquire, Province of Tarapacá.

that it contained a large proportion of magnesium sulphate. Analyses of two different samples yielded:

	Found.		Calculated for (Cu, Mg)SO ₄ +5H ₂ O :
	I.	II.	
Sulphur trioxide.....	35.74%	35.67%	35.84%
Cupric oxide.....	12.41	12.46	11.89
Magnesium oxide.....	11.42	11.36	11.95
Ferrous oxide.....	.97	1.05	
Manganous oxide.....	.23	.41	
Nickel oxide.....	trace	.06	
Water	38.45	38.31	40.32
	99.22%	99.32%	100.00%

The conclusions to be drawn from these results are, first, that the mineral is an isomorphous mixture of the sulphates of copper and magnesium; secondly, that this double salt contains five molecules of water of crystallization; and thirdly, that for each molecule of copper sulphate there are present (very nearly) two molecules of magnesium sulphate. The shortage in the water content is doubtless owing to efflorescence, and there should be credited to the magnesia content an amount equivalent to the percentages of the oxides of iron and manganese.

Under the name of cupromagnesite a double sulphate of copper and magnesium has been described by Scacchi. It occurs in the form of green crusts on lava from the Vesuvius, and is believed to be isomorphous with melanterite, containing, like the latter, seven molecules of water of crystallization. I have seen no reference to a mineral of the same composition as that above described.

Associated with the chalcantite and the double sulphate of copper and magnesium were other little masses, dirty-white in color and more or less stained with ferric oxide. They were very hard and consisted almost entirely of silica, containing only trifling amounts of oxide of iron and magnesia. It is puzzling to explain why these masses should simulate the form of the accompanying soluble sulphates.

BROCHANTITE(?) CONTAINING ARSENIC ACID.

Very small quantities only were available of an emerald green mineral which was observed partly in fine acicular crystals dissemi-

nated through a silicious rock, and partly as an incrustation upon quartz. On account of its physical characters, as well as the strong reaction its solution gave with barium chloride, I was first inclined to regard it as a typical brochantite. This impression was confirmed by rough estimations of the copper and sulphur trioxide, but as these tests had been made on impure material, I decided to attempt the analysis of a carefully prepared sample. To obtain about .5 gm. of the substance, I found it necessary to sacrifice the best specimens in my possession, and my patience was put to a severe test in picking the minute crystals under the lens. They were sorted over and over until the microscope showed only a few remaining specks of quartz adhering to the larger crystals of the copper mineral.

The quartz material from which this sample had been picked still contained considerable quantities of the copper mineral, and it occurred to me that it might serve for a qualitative, and, perhaps, a preliminary quantitative analysis. Accordingly the material was extracted with hydrochloric acid, and the resulting green solution divided into equal parts. When the copper had been precipitated with hydrogen sulphide, it was noticed that yellow flakes began to form, and after the liquid saturated with the gas had been allowed to stand in a warm place over night, a considerable amount of the yellow precipitate had settled on the black copper sulphide. There could be no doubt, then, that arsenic was present in the form of arsenic acid. The sulphides were separated and worked up in the usual manner, and the filtrate was searched for other metallic ions. It yielded only traces of iron oxide and alumina. The other half of the original solution was used for the determination of the sulphur trioxide and the arsenic acid. The results of the determinations, calculated for the entire amount of copper mineral dissolved, gave:

Copper5068 grms.
Sulphur trioxide0783 grms.
Arsenic anhydride1309 grms.

The question now arose as to whether the very large proportion of arsenic acid found really constituted an integral part of the supposed brochantite, or whether it did not belong to another mineral contained in the rock. The test previously made seemed to preclude such an arsenic content of the mineral under examination.

In view of the very limited amount of material available for analysis, it seemed best to dispense with the water determination and confine the characterization of the mineral to ascertaining the specific gravity and an estimation of the base and the acids. The following results were obtained:

Specific gravity	3.160	
	I.	II.
	Per Cent.	Per Cent.
Sulphur trioxide	16.32	16.63
Arsenic anhydride	2.31	2.40
Copper oxide	68.90	68.68
Silica	1.63	1.18

If we deduct the quartz from the substance taken for analysis, the percentages of sulphur trioxide and oxide of copper will be found to approach very nearly to those in brochantite which contains:

	Per Cent.
Sulphur trioxide	17.7
Cupric oxide	70.3
Water	12.0

and it is difficult to explain the rôle of the arsenic acid which is equivalent to about 4.4 per cent. of sulphur trioxide. To establish a definite formula for the compound it would be necessary to ascertain by further analyses whether or not the proportion of arsenic anhydride is constant, and to complete the analysis by an exact determination of the water. The specimens in my possession, unfortunately, are not sufficient for this purpose.

The specimens were collected at Copaquire, Province of Tarapacá.

ATACAMITE.

In conclusion I desire to call attention to some magnificent specimens of atacamite from Paposo in the Province of Antofagasta. They do not show the usual slender prisms, but consist of aggregates of fairly large crystals, closely resembling the octahedron of the isometric system modified by the cube and the rhombic dodecahedron. On closer examination, however, it would seem that they are really combinations such as have been observed on the atacamite



FIG. 1. Atacamite from Paposo, Chile.

from certain localities in South Australia.⁴ As was to be expected, the analysis showed the specimens to be an atacamite of unusual purity and of normal composition. It yielded:

Sp. gr.	3.738	
	Found.	Calculated for
	Per Cent.	$\text{CuCl}_2 \cdot 3\text{Cu}(\text{OH})_2$.
		Per Cent.
Chlorine	16.51	16.6
Copper	14.79	14.9
Cupric oxide	55.28	55.8
Water	12.42	12.7
Insol.79	
	<hr/> 99.79	<hr/> 100.0

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⁴I hope to verify this by actual measurement.